

We claim:

1. A method of making a crosslinked polymer comprising the steps of:
 - a) providing a highly fluorinated polymer comprising pendent groups which include a group according to the formula $\text{-SO}_2\text{X}$, wherein each X is independently selected from F, Cl, Br, I, -OH or $\text{-O-SO}_2\text{R}^2$ wherein R^2 is an aliphatic group containing 1-18 carbon atoms which may be substituted; and
 - b) reacting said polymer with a crosslinking agent according to the formula Ar_nR^1 , wherein each Ar is selected independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be substituted, wherein R^1 is a direct bond or an aromatic or aliphatic linking group, wherein R^1 may be straight-chain, branched, cyclic, heteroatomic, polymeric, halogenated, fluorinated or substituted, and where n is at least 2, to form crosslinks.
2. The method according to claim 1 wherein said crosslinks comprise units according to the formula $(\text{-SO}_2\text{Ar})_n\text{R}^1$.
3. The method according to claim 1 wherein said method additionally comprises, prior to said step b), the step of:
 - c) forming said polymer into a membrane.
4. The method according to claim 3 wherein said membrane has a thickness of 90 microns or less.
5. The method according to claim 1 wherein said method additionally comprises, after said step b), the step of:
 - d) converting any remaining groups according to the formula $\text{-SO}_2\text{X}$ to sulfonic acid groups.

6. The method according to claim 1 wherein each Ar is a phenyl group which may be substituted.

7. The method according to claim 1 wherein one or more Ar is substituted with an
5 electron donating group.

8. The method according to claim 1 wherein one or more Ar is substituted with an alkoxy group.

10 9. The method according to claim 1 wherein R^1 is an aliphatic linking group containing 1-20 carbon or oxygen atoms.

10. The method according to claim 1 wherein R^1 is $-O-R^3-O-$, where R^3 is an aliphatic linking group containing 1-18 carbon or oxygen atoms.

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11. The method according to claim 1 wherein n is 2.

12. The method according to claim 1 wherein said step b) of reacting said polymer with a crosslinking agent is carried out in the presence of a catalyst such as a Lewis
20 acid.

13. The method according to claim 1 wherein each X is independently selected from F or Cl.

25 14. The method according to claim 1 wherein said pendent groups are according to the formula $-O-(CF_2)_4-SO_2X$.

15. The method according to claim 1 wherein said pendent groups are according to the formula $-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_2X$.

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16. The method according to claim 1 wherein step a) of providing a highly fluorinated polymer comprises the steps of:

e) providing a highly fluorinated polymer comprising pendent groups which include a group according to the formula $-\text{SO}_2\text{F}$; and

5 f) converting at least a portion of said $-\text{SO}_2\text{F}$ groups to $-\text{SO}_2\text{Cl}$.

17. The method according to claim 16 wherein step f) of converting at least a portion of said $-\text{SO}_2\text{F}$ groups to $-\text{SO}_2\text{Cl}$ is accomplished by reduction of the $-\text{SO}_2\text{F}$ group to $-\text{SO}_2\text{H}$ followed by conversion to $-\text{SO}_2\text{Cl}$ by reaction with hypochloride.

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18. The method according to claim 16 wherein step f) of converting at least a portion of said $-\text{SO}_2\text{F}$ groups to $-\text{SO}_2\text{Cl}$ is accomplished by reaction with oxalylchloride.

15 19. The method according to claim 1 wherein step a) of providing a highly fluorinated polymer comprises the steps of:

e) providing a highly fluorinated polymer comprising pendent groups which include a group according to the formula $-\text{SO}_2\text{F}$; and

f) converting at least a portion of said $-\text{SO}_2\text{F}$ groups to $-\text{SO}_2\text{-O-SO}_2\text{R}^2$,

20 wherein R^2 is an aliphatic group containing 1-18 carbon atoms which may be substituted.

20. A highly fluorinated crosslinked polymer comprising: a backbone, pendent groups which comprise sulfonic acid groups, and crosslinks comprising units according to the formula $(-\text{SO}_2\text{Ar})_n\text{R}^1$ wherein each Ar is selected independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be substituted, wherein R^1 is a direct bond or an aromatic or aliphatic linking group, wherein R^1 may be straight-chain, branched, cyclic, heteroatomic, polymeric, halogenated, fluorinated or substituted, and where n is at least 2.

21. A polymer electrolyte membrane comprising the highly fluorinated crosslinked polymer according to claim 20.
- 5 22. The polymer electrolyte membrane according to claim 21 having a thickness of 90 microns or less.
23. The polymer according to claim 20 wherein each Ar is a phenyl group which may be substituted.
- 10 24. The polymer according to claim 20 wherein one or more Ar is substituted with an electron donating group.
- 15 25. The polymer according to claim 20 wherein one or more Ar is substituted with an alkoxy group.
26. The polymer according to claim 20 wherein R^1 is an aliphatic linking group containing 1-20 carbon or oxygen atoms.
- 20 27. The polymer according to claim 20 wherein R^1 is $-O-R^3-O-$, where R^3 is an aliphatic linking group containing 1-18 carbon or oxygen atoms.
28. The polymer according to claim 20 wherein n is 2.
- 25 29. The polymer according to claim 20 wherein said pendent groups are according to the formula $-O-(CF_2)_4-SO_3H$.
30. The polymer according to claim 20 wherein said pendent groups are according to the formula $-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H$.

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31. The polymer according to claim 20 having an equivalent weight of less than 1200.
32. A method of making a crosslinked polymer comprising the steps of:
- 5 a) providing a highly fluorinated polymer comprising first pendent groups which include a group according to the formula $\text{-SO}_2\text{X}$, wherein each X is independently selected from F, Cl, Br, I, -OH or $\text{-O-SO}_2\text{R}^2$ wherein R^2 is an aliphatic group containing 1-18 carbon atoms which may be substituted, and second pendent groups which include groups -Ar , wherein each Ar is selected
- 10 independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be substituted; and
- b) reacting said polymer to form crosslinks between said first and second pendent groups.
- 15 33. The method according to claim 32 wherein said crosslinks comprise units according to the formula $\text{-SO}_2\text{Ar-}$.
34. The method according to claim 32 wherein said method additionally comprises, prior to said step b), the step of:
- 20 c) forming said polymer into a membrane.
35. The method according to claim 34 wherein said membrane has a thickness of 90 microns or less.
- 25 36. The method according to claim 32 wherein said method additionally comprises, after said step b), the step of:
- d) converting any remaining groups according to the formula $\text{-SO}_2\text{X}$ to sulfonic acid groups.
- 30 37. The method according to claim 32 wherein each Ar is a phenyl group which may be substituted.

38. The method according to claim 32 wherein one or more Ar is substituted with an electron donating group.

5 39. The method according to claim 32 wherein one or more Ar is substituted with an alkoxy group.

40. The method according to claim 32 wherein said step b) of reacting said polymer is carried out in the presence of a catalyst such as a Lewis acid.

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41. The method according to claim 32 wherein each X is independently selected from F or Cl.

42. The method according to claim 32 wherein said first pendent groups are
15 according to the formula $-\text{O}-(\text{CF}_2)_4-\text{SO}_2\text{X}$.

43. The method according to claim 32 wherein said first pendent groups are according to the formula $-\text{O}-\text{CF}_2-\text{CF}(\text{CF}_3)-\text{O}-\text{CF}_2-\text{CF}_2-\text{SO}_2\text{X}$.

20 44. The method according to claim 32 wherein step a) of providing a highly fluorinated polymer comprises the steps of:

e) providing a highly fluorinated polymer comprising first pendent groups which include a group according to the formula $-\text{SO}_2\text{F}$; and

f) converting at least a portion of said $-\text{SO}_2\text{F}$ groups to $-\text{SO}_2\text{Cl}$.

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45. The method according to claim 44 wherein step f) of converting at least a portion of said $-\text{SO}_2\text{F}$ groups to $-\text{SO}_2\text{Cl}$ is accomplished by reduction of the $-\text{SO}_2\text{F}$ group to $-\text{SO}_2\text{H}$ followed by conversion to $-\text{SO}_2\text{Cl}$ by reaction with hypochloride.

46. The method according to claim 44 wherein step f) of converting at least a portion of said -SO₂F groups to -SO₂Cl is accomplished by reaction with oxalylchloride.

- 5 47. The method according to claim 32 wherein step a) of providing a highly fluorinated polymer comprises the steps of:
- e) providing a highly fluorinated polymer comprising first pendent groups which include a group according to the formula -SO₂F; and
 - f) converting at least a portion of said -SO₂F groups to -SO₂-O-SO₂R²,

10 wherein R² is an aliphatic group containing 1-18 carbon atoms which may be substituted.

48. The method according to claim 32 wherein said highly fluorinated polymer comprises a greater number of first pendant groups than second pendant groups.

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49. A highly fluorinated crosslinked polymer comprising: a backbone, pendent groups which comprise sulfonic acid groups, and crosslinks comprising units according to the formula -SO₂Ar- wherein each Ar is selected independently from aromatic groups containing 6-24 carbon or nitrogen atoms and wherein each Ar may be

20 substituted.

50. A polymer electrolyte membrane comprising the highly fluorinated crosslinked polymer according to claim 49.

25 51. The polymer electrolyte membrane according to claim 50 having a thickness of 90 microns or less.

52. The polymer according to claim 49 wherein each Ar is a phenyl group which may be substituted.

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53. The polymer according to claim 49 wherein one or more Ar is substituted with an electron donating group.

54. The polymer according to claim 49 wherein one or more Ar is substituted with an alkoxy group.

55. The polymer according to claim 49 wherein said first pendent groups are according to the formula $-O-(CF_2)_4-SO_3H$.

56. The polymer according to claim 49 wherein said first pendent groups are according to the formula $-O-CF_2-CF(CF_3)-O-CF_2-CF_2-SO_3H$.

57. The polymer according to claim 49 having an equivalent weight of less than 1200.

58. The method according to claim 3 wherein step c) comprises imbibing said mixture into a porous supporting matrix.

59. The method according to claim 58 wherein said porous supporting matrix is a porous polytetrafluoroethylene web.

60. The method according to claim 34 wherein step c) comprises imbibing said mixture into a porous supporting matrix.

61. The method according to claim 60 wherein said porous supporting matrix is a porous polytetrafluoroethylene web.

62. The polymer electrolyte membrane according to claim 21 wherein said intimate mixture is embedded in a porous supporting matrix.

63. The polymer electrolyte membrane according to claim 62 wherein said porous supporting matrix is a porous polytetrafluoroethylene web.
64. The polymer electrolyte membrane according to claim 50 wherein said intimate
5 mixture is embedded in a porous supporting matrix.
65. The polymer electrolyte membrane according to claim 64 wherein said porous supporting matrix is a porous polytetrafluoroethylene web.